Development of New Negative-tone Molecular Resists Based on Phenylcalix [4] resorcinarene for EUVL.

Investigation of correlation with the octanol water partition coefficient and the sensitivity of negative-tone molecular resists

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Motivation for Negative-Tone Resist

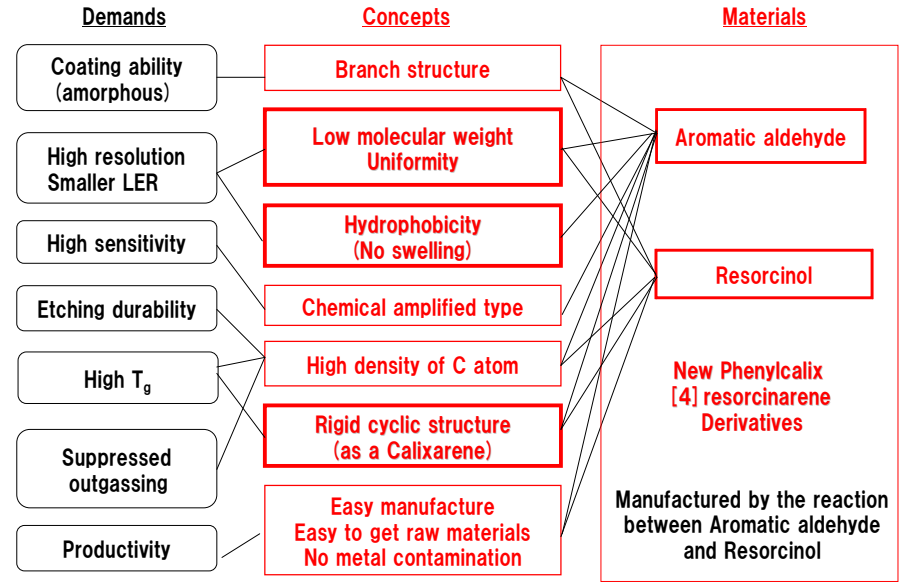
2007 ITRS Roadmap

Table LITH4a Resist Requirements—Near-term

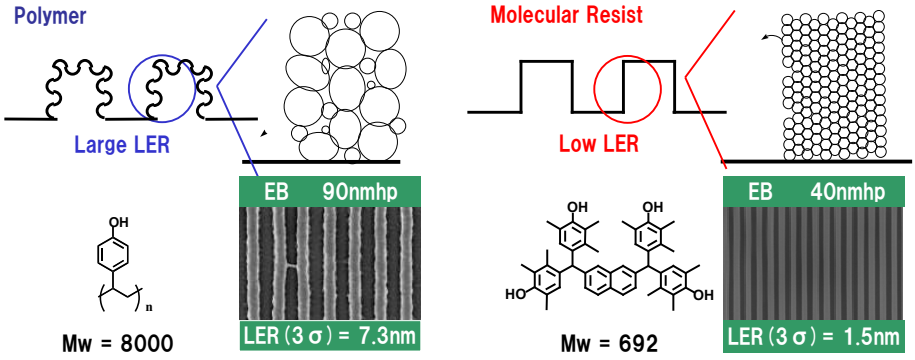
Year of Production	2007	2008	2009	2010	2011	2012	2013	2014	2015
DRAM ½ pitch (nm) (contacted)	65	57	50	45	40	36	32	28	25
Flash ½ pitch (nm) (un-contacted poly)	53.5	45.0	40.1	35.7	31.8	28.3	25.3	22.5	20.0
MPU gate in resist length (nm)	39	32	28	30	40	36	21	28	25
	23	20	18		16	14		11	10
Resist Characteristics *									
Resist meets requirements for gate resolution and gate CD control (nm, 3 sigma) **†	2.6	2.3	2.1	1.9	1.7	1.5	1.3	1.2	1.0
Resist thickness (nm, single layer) ***	105-190	90-160	80-145	70-130	60-115	55-100	50-90	45-80	40-75
PEB temperature sensitivity (nm/C)	1.75	1.5	1.5	1.5	1.5	1.5	1	1	1
Backside particle density (particles/cm^2)	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Back surface particle diameter: lithography and measurement tools (nm)	120	120	100	100	100	100	75	75	75
Defects in spin-coated resist films (#/cm^2) †	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Minimum defect size in spin-coated resist films (nm)	40	35	30	30	20	20	20	20	10
Defects in patterned resist films, gates, contacts, etc. (#/cm^2)	0.04	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.01
Minimum defect size in patterned resist (nm)	40	35	30	30	20	20	20	20	10
LWR (3sigma) <8% of CD	3.4	3.0	2.7	2.4	2.1	1.9	1.7	1.5	1.3
Defects in spin-coated resist films for double patterning (#/cm^2)	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Backside particle density for double patterning (#/cm^2)	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14

Negative-tone resists are limitedly influenced by flare.
We believe Negative-tone resist can achieve these required properties.

Design Concepts for New Negative-tone Molecular Resist Material



Motivation for negative-tone molecular resist

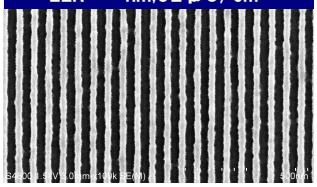


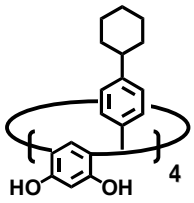
- Phenylcalix [4] resorcinarenes are small-size and high-Tg molecules, enough for patterning high-resolution and low-LER.

Our proposal for molecular resist materials.
M. Echigo et al., *5th International EUV Symposium*, **01-RE-27** (2006)

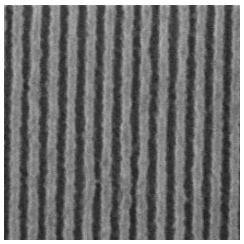
Previous Data
(Negative-tone resist using MGR108)

EB 30nm hp,60nmt
LER=--nm,52 μC/cm²





MGR108

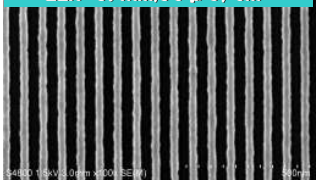
EUV LS Pattern	
CD (nm)	26
Esize (mJ/cm²)	24.0
LWR (nm)	6.1
nZ (32)	12.8

By courtesy of SEMATECH

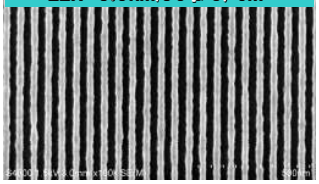
- Patterns were well defined at ≦30 nmhp.

Previous Data
(Negative-tone resist using CRA-02)

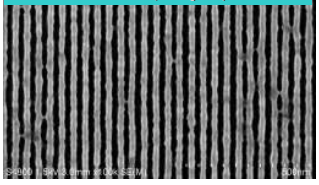
EB 40nm hp,55nmt
LER=3.4nm,90 μC/cm²

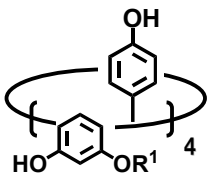


EB 30nm hp,55nmt
LER=3.0nm,90 μC/cm²



EB 25nm hp,55nmt
LER=4.1nm,90 μC/cm²





CRA-02

- Patterns were well defined at 40-25 nmhp.

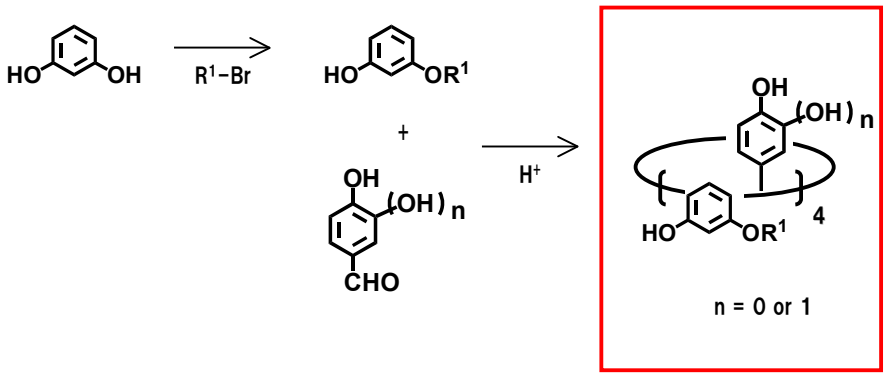
The purpose of this study

Investigation of correlation with **the octanol water partition coefficient (ClogP)** and **the sensitivity at a dose of 50 nmhp** of negative-tone molecular resists.

The octanol water partition coefficient logP is used in QSAR studies and rational drug design as a measure of molecular hydrophobicity.
Hydrophobicity affects drug absorption, bioavailability, hydrophobic drug-receptor interactions, metabolism of molecules, as well as their toxicity.
LogP has become also a key parameter in studies of the environmental fate of chemicals.

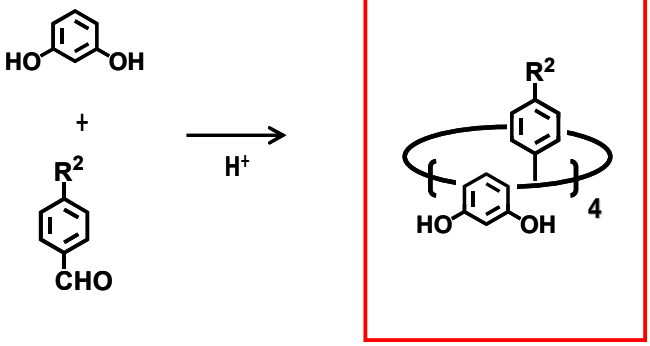
The values of the octanol water partition coefficient were measured by **ChemProp Pro for Chem 3D**.

General synthesis of HP-CRA



Six HP-CRA derivatives as a mixture of various isomers were synthesized in high yields (99%).

General synthesis of AP-CRA



Two AP-CRA derivatives as a mixture of various isomers were synthesized in high yields (99%).

Experiment (Resist composition)

	Matrix	PAG	Cross-Linker	Quencher	Solvent
Resist A	HP-CRA-01	PAG-1	HMMM	Q-1	PGME
Resist B	HP-CRA-02				
Resist C	HP-CRA-03				
Resist D	HP-CRA-04				
Resist E	HP-CRA-05				
Resist F	HP-CRA-06				
Resist G	AP-CRA-07				
Resist H	AP-CRA-08				

PAG-1 : sulfonium sulfonate
HMMM : hexamethoxymethylmelamine
Q-1 : amine
PGME : propylene glycol monomethyl ether

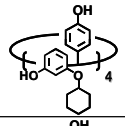
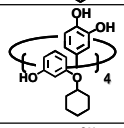
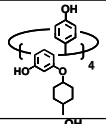
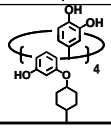
Experiment (EB Patterning Evaluations)

Apparatus:
Ultra－High Precision EB Lithography System
(ELS－7500 : Acceleration Voltage 50 keV)
at Mitsubishi Gas Chemical (MGC)

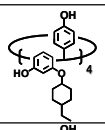
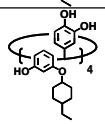
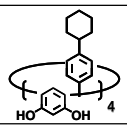
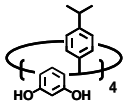
Process Conditions:
Substrate: Organic layer (UL)
Film Thickness: 30－60nm
PB＆PEB: 110℃/90s
Dev.: TMAH 0.26N 60s

Analysis Conditions:
SEM: S4800

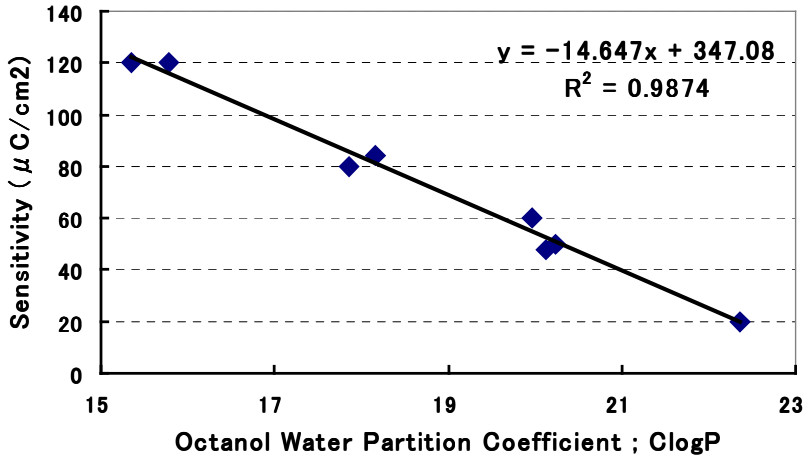
Characteristics of CRAs (1/2)

Matrix	Model Structure	Dissolution rate (nm/min)	ClogP	Sensitivity (μC/cm²)
HP-CRA-01		> 50	18.16	84
HP-CRA-02		> 50	15.78	120
HP-CRA-03		> 50	20.24	50
HP-CRA-04		> 50	17.85	80

Characteristics of CRAs (2/2)

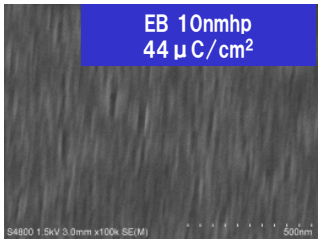
Matrix	Model Structure	Dissolution rate (nm/min)	ClogP	Sensitivity (μC/cm²)
HP-CRA-05		> 50	22.36	20
HP-CRA-06		> 50	19.97	60
AP-CRA-07		> 50	20.12	48
AP-CRA-08		> 50	15.35	78

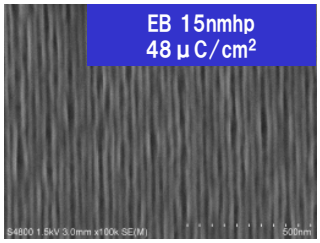
Correlation between the octanol water partition coefficient and the sensitivity

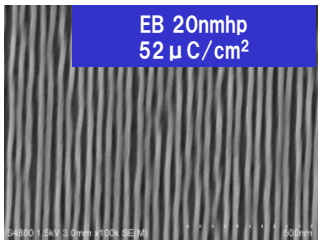


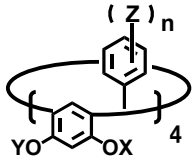
The sensitivity of resists were higher as the value of the octanol water partition coefficient got smaller.

Highlight Data (New Resist) - Update -









calix [4] resorcinarene derivative

- By using new calix [4] resorcinarene derivative, sub 30nm hp patterns were resolved at the high sensitivity

Summary

- We invested of correlation with the octanol water partition coefficient and the sensitivity of negative-tone molecular resists based on calix [4] resorcinarene (CRA) by Electron Beam Lithography (EBL).

- The sensitivity of negative-tone molecular resists were higher as the value of the octanol water partition coefficient got smaller.

- It was confirmed that the octanol water partition coefficient was useful to the guess of sensitivity of negative-tone molecular resists.

- Furthermore, we have developed new calix [4] resorcinarenes showing well-defined sub 20nm half-pitch patterns.

- Future study is underway to improve resist performance through material and process optimization to evaluate resist performance by EUV lithography (EUVL).